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Synchrotron-Radiation-based Investigations of the Electronic Structure of Pu

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Abstract

Synchrotron radiation from the Advanced Light Source has been used to investigate the electronic structure of α- Pu and δ- Pu . Measurements include core level and valence band photoelectron spectroscopy, Resonant Photoelectron Spectroscopy (REPES), and X-ray Absorption Spectroscopy (XAS).

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I.   Introduction

The valence electronic structures of the actinide metals and alloys in general and plutonium (Pu) in particular remain mired in controversy. [1-5] Interestingly, the various phases of Pu metal provide a microcosm of the metallic actinides as a whole. [6-9] Thus, unraveling the nuances of the interplay of electronic and geometric structures in Pu will illuminate the properties of all transuranic metals.   In a sense, the behavior of the Pu 5f electrons is completely counter-intuitive. The dense phase, α, has some semblance of delocalization in the 5f valence bands and thus should be more easily treated theoretically within single electron models such as the Local Density Approximation (LDA), although the complexity of the unit cell (16 atoms) and the large spin-orbit splitting of the 5f states can cause difficulties [4]. The α phase is monoclinic, which is a low symmetry ordering. [10] The less dense δ-phase is fcc and exhibits evidence of localized and/or correlated electronic behavior. The fcc is a high symmetry phase which is normally associated with superior wavefunction overlap in d state metals. But herein lies one insight: the linear combinations of the 5f's do not produce the nicely lobed wavefunctions with symmetry about the x, y, z and diagonal axes, as occurs for d states. Instead, the linear combinations of   f -states have oddly lobed and badly directed wavefunctions [11-13], which match very poorly with the high symmetry of the fcc structure. In the rare earths and lanthanides, this odd lobing is of no consequence: generally, the 4f valence states are inside the outer 5d, 6p and 6s electrons and can be treated as isolated, atomic-like orbitals that do not participate in chemical bonding. In the actinides, the 5f's are less well shielded.   Shielding is undoubtedly a key issue and relates to the volume changes. In fact, the 20% volume increase of Pu between the α and δ phases is a reflection of the discontinuous 30% volume jump between Pu and Am, as one moves along the row of actinide elements. [14-16] Furthermore, the

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fcc δ- Pu can not be treated theoretically within single electron calculations without severe ad hoc corrections [4,5], e.g., the addition of Coulombic repulsion terms to LDA formalisms. Finally, we have not even begun to deal with the issue of dilute alloy formation and its impact upon the electronic structure of metallic actinides. The upshot of this is that the valence electronic structure of Pu in particular and the actinides in general is only poorly understood. To attempt to correct this situation, we have begun a series of synchrotron-radiation-based, photoelectron spectroscopy investigations at the Advanced Light Source in Berkeley, CA.

II.   Experimental Details

The Pu 5f valence and conduction band measurements were performed using Photoelectron Spectroscopy (PES) and X-ray Absorption Spectroscopy (XAS). One variant of PES is resonant photoemission. In a ResPes experiment, the valence band spectrum is collected as the photon energy is ramped through a core level absorption edge. In the case of Pu, the photon energy was scanned through the $O_{4,5}$ (5d) absorption edge. Thus, the result is the 5d5f5f resonant photoemission decay from Pu metal. The final state can be reached by an x-ray absorption - Coulomb decay process, $5d^{10} 5f^n + h\nu \rightarrow 5d^9 5f^{n+1} \leftrightarrow 5d^{10} 5f^{n-1} + e$, and by direct photoemission, $5d^{10} 5f^n + h\nu \rightarrow 5d^{10} 5f^{n-1} + e$, where e is a photoelectron in a continuum state which has no interaction with the ionic state left behind. Interference between the different pathways results in asymmetric absorption features in the measured spectra.

The experiments were performed at the Spectromicroscopy Facility (Beamline 7.0) at the Advanced Light Source in Berkeley, CA. [17].

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Figure 1: Aerial view of the Advanced Light Source at Lawrence Berkeley Laboratory in Berkeley, CA.

The measurements were made at the SpectroMicroscopy Facility (SMF) of the ALS, based at Beam-Line 7.0. The SMF Participating Research Team, which helped develop BL7 in concert with LBNL personnel, had a longstanding interest in actinide research: First results from BL7 included PES of the Cm 4f levels, as shown in Figure 2. Also shown in Figure 3 is a layout of BL7. The Pu measurements were performed in the ultra-ESCA spectrometer.
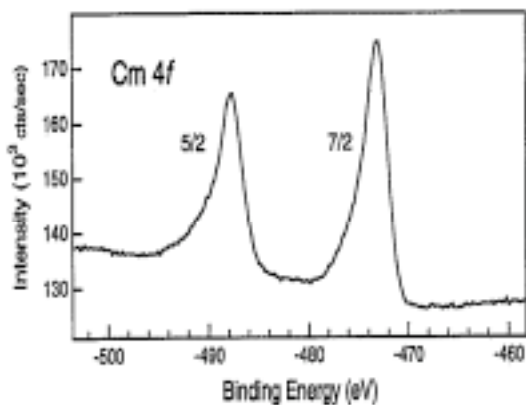

Figure 2.   PES spectrum of the Cm 4f levels, obtained with a photon energy of 1040 eV. An estimated 3 nanograms of curium oxide was excited by the approximately 50 micrometer diameter beam spot. Taken from Ref 17.

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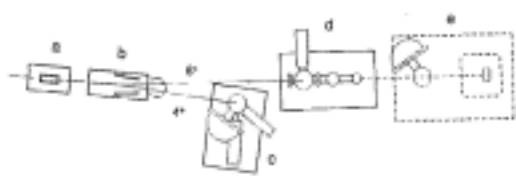# of the Electronic Structure of Pu

Figure 3   Layout of the SpectroMicroscopy Facility including (a) vertical refocusing optics, (b) horizontal refocusing optics, (c) ultraESCA, (d) x-ray fluorescence and (e) Scanning Photo-Electron Microscope (SPEM). Taken from Reference 17.

Based upon standard mean free path arguments, the sampling depth should be on the order of 20 to 50 angtroms. The Pu samples were taken from a specially purified batch of Pu metal. The plutonium was zone refined and vacuum distilled while magnetically levitated [18] . The product of the purification process was α-Pu containing a total of 170 ppm impurities. A portion of the refined metal was alloyed with gallium to form the δ-phase (fcc symmetry). The sample surfaces were prepared by repeated room-temperature, sputter-annealing cycles to minimize the amount of oxygen and other impurities dissolved in the sample or at grain boundaries, in a specially designed chamber attached to the sample introduction and analysis systems on Beamline 7.0. The transfer, preparation, and analysis chambers ensured that the Pu metal samples were always under vacuum, to minimize any surface contaminants that could adversely effect the soft x-ray measurements.

III   RESPES Results

Photoelectron spectroscopy is a "photon in, electron out" process. Often, it can be simplified down to a single electron phenomenon, where the energy of the photon is absorbed and transferred over entirely to a single electron, while all other "spectator" electrons essentially remain frozen. An advantage of this is its simplicity of interpretation. But in many systems, it is possible to induce a process with heightened sensitivity and significantly increased cross sections: resonant photoemission (ResPes). [19-22] Here, a second set of indirect channels open up, which contribute in concert with the

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original or direct channel of simple photoemission. Shown in Figure 4 are resonant photoemission results from polycrystalline α-Pu and single crystallite (large grain polycrystalline) δ-Pu.
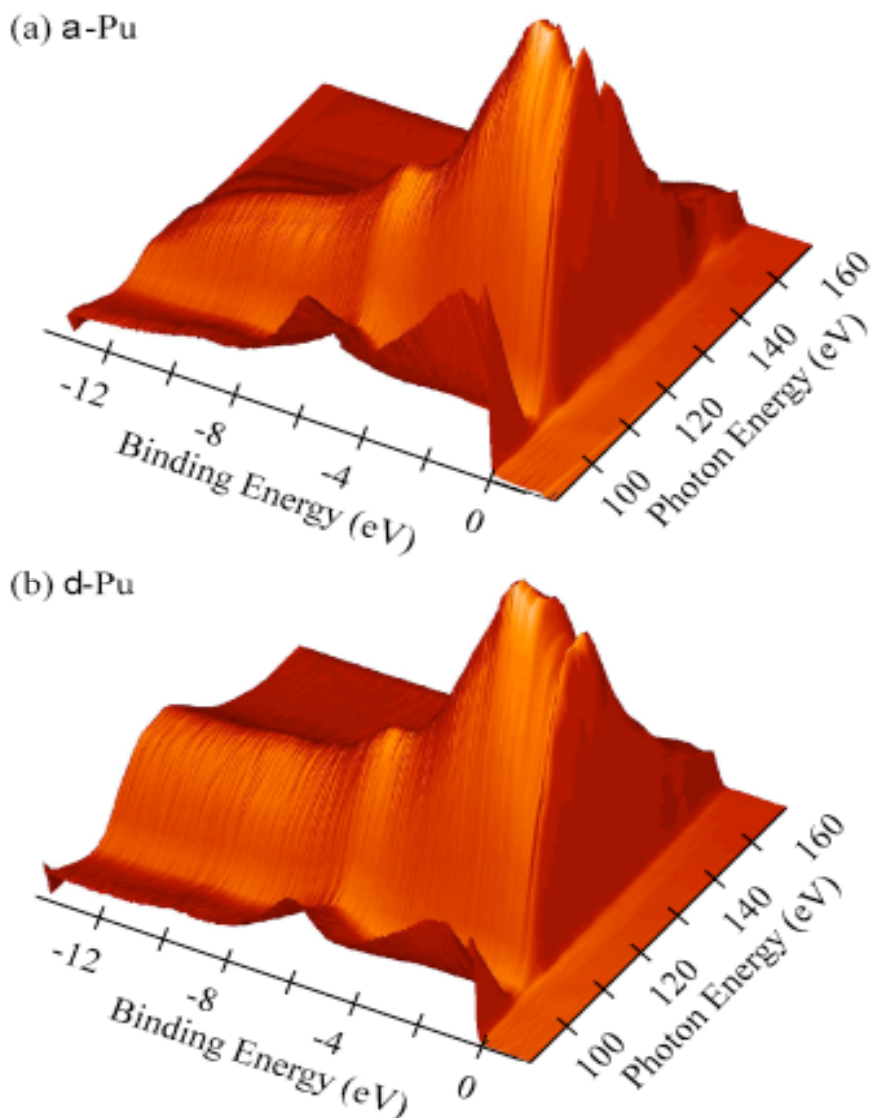
(a) a-Pu

(b) d-Pu

Figure 4: Two Resonant Photoemission (ResPes) data sets are shown here, for a polycrystalline α (top) and single crystallite δ (bottom). The plots show the intensity variations (z axis) versus the binding energy of the states (the negative numbers in eV; zero is the Fermi energy) and photon energy (between 90eV and 160eV). As will be discussed below, the α sample probably had a δ-like reconstruction on the surface.

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The plots show intensity variations versus binding energy and photon (excitation) energy. Along the photon energy axis (90 eV to 160eV), the classical signature of resonant photoemission can be seen: an anti-resonance or intensity minimum (near 100eV) followed by a maximum (near 125 eV). These energies correlate with the Pu 5d core level threshold at 102eV: ResPes is a multielectron process which in this case involves 5d as well as 5f electrons. Along the binding energy axis, the "wall" is the threshold associated with the Fermi energy: no emission can occur above the Fermi Energy. The overall spectral envelopes are approximately the same, as expected for two samples which are primarily Pu. Subtle yet significant differences can be observed between the α and single crystallite δ samples, particularly at the Fermi energy and near a photon energy of 130eV. These results suggest that the valence electronic structure of Pu is dependent upon its phase and chemical state. Nevertheless, overall the two sets of spectra strongly resemble each other and confirm the observation of Pu 5f ResPes.

IV   PES and XAS

Additional measurements, such as XAS, wide scan and core level PES of the Pu and tracking of oxygen surface contamination, have been performed. Shown in Figure 5 are the $O_{4,5}$, XAS and 4f core level PES data for both Pu samples. Here it is clear that there are obvious differences between the α and δ spectra, which may be used to differentiate between the phases. It should be noted that these spectra confirm earlier work performed by T. Gouder et al. [23] and others [24-26] using laboratory sources to perform core level PES. These spectra are sensitive to the bulk: it seems fairly likely that surface effects are not the dominant factor here since the kinetic energy is close to 400eV and provides substantial bulk sensitivity. It has been argued in the past [23] that the relative sharpness of the peaks in α-Pu PES and the large satellite

features in δ-Pu PES are suggestive of delocalization in α-Pu and atomic or electron correlated effects in δ-Pu. (For more information about the X-ray absorption of the Pu O$_{4,5}$, (5d -> 5f) transition, please see Reference 27.)
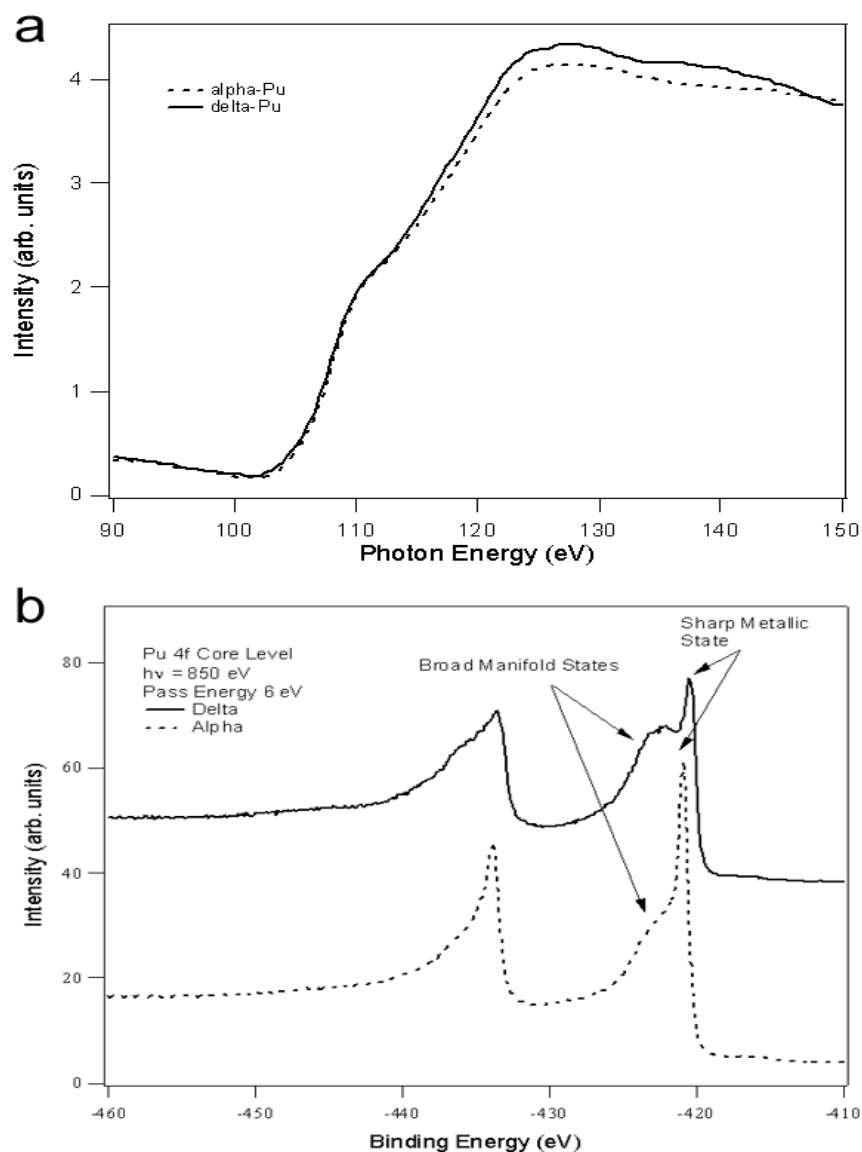

Figure 5 *X-ray absorption (O $_{4,5}$, 5d -> 5f transition) and Pu 4f core level spectroscopy. The PES spectra were collected with a photon energy of 850 eV. Note that two large components are visible in each spectrum, a sharp feature at low binding energy and a broad feature at higher binding energy.*

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An added complication is that the α-Pu sample probably had a δ-like reconstruction on its surface. [28]

Interestingly, while the Pu 4f core level spectra (Figure 5b) are consistent with previous results, the surface contamination work has lead to a surprising result, relative to previous laboratory studies (Figure 6).
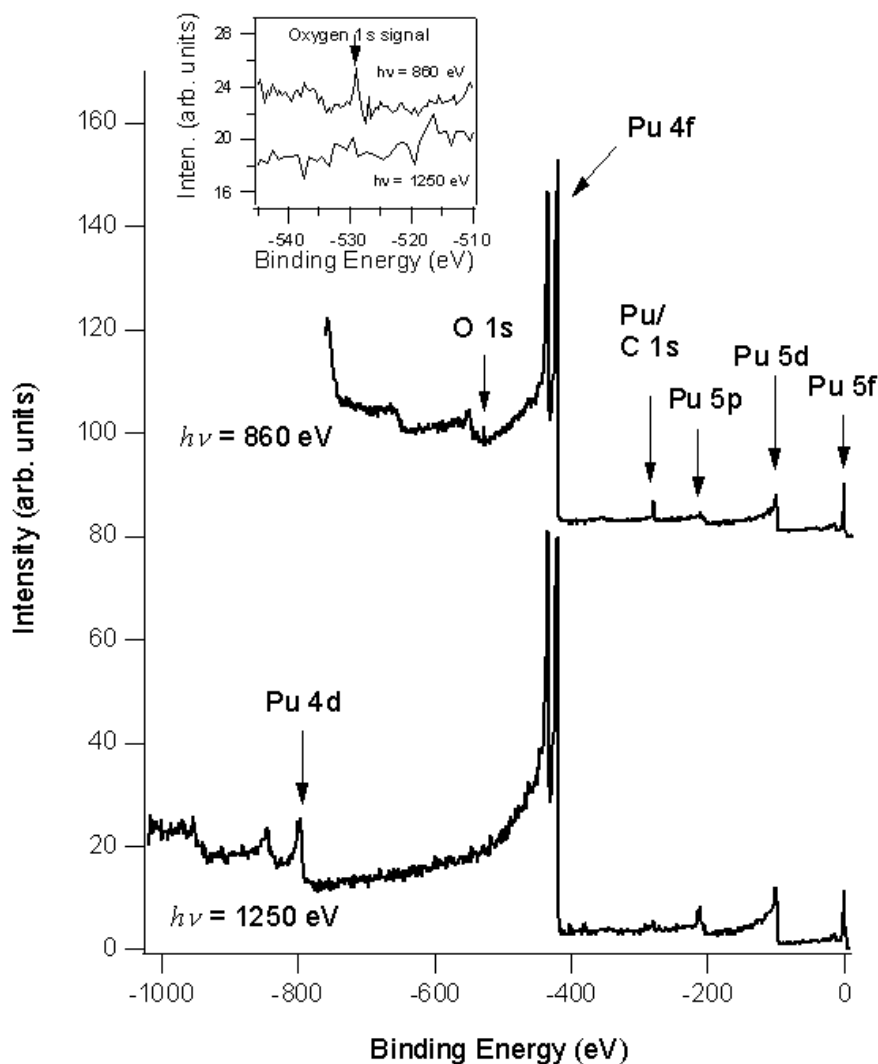

Figure 6   Wide scan PES of Pu, including a blowup of the oxygen 1s region. The oxygen peak (binding energy of -530 eV) is much more easily observed at 860eV than at 1250eV.

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Here the spectra at a photon energy of 1250 eV (i.e. approximately Mg Kα energy) suggests that the sample surface is "clean," but the spectrum at a photon energy of 860eV indicates the presence of oxygen contamination. The increased sensitivity of the measurements made at photon energies available only at synchrotron radiation sources illustrates the importance of true photon energy tunabilty. (For more information about Pu RESPES and the determination of the oxygen levels in these samples, please see Reference 28.)

X-ray absorption spectroscopy has also been performed at higher energies, using α-Pu. At the $N_{4,5}$, edges, it is possible to observe the separate 5/2 and 3/2 peaks, as shown in Figure 7 below. (For more information about Pu $N_{4,5}$, XAS, please see Reference 29.)
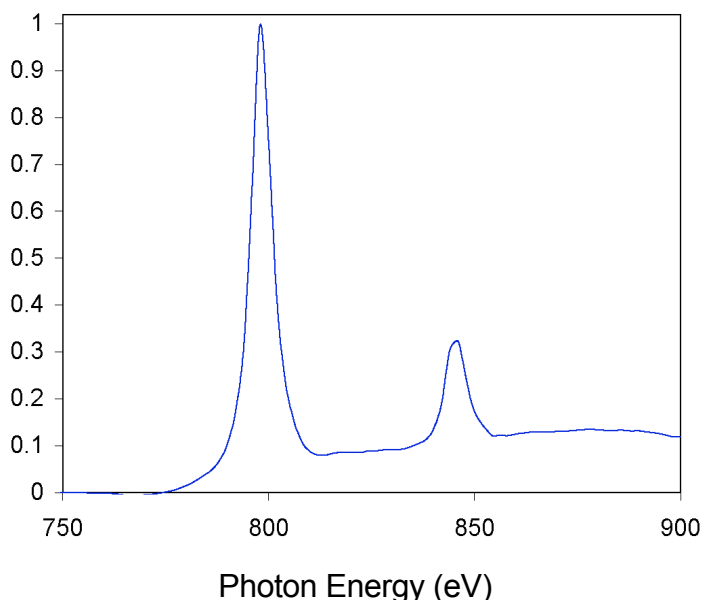

Photon Energy (eV)

Figure 7   X-ray absorption ($N_{4,5}$, 4d -> 5f transition), showing the 4d$_{5/2}$ white line near 800 eV and the 4d$_{3/2}$ whiteline near 850 eV. The sample was α-Pu.

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V   Conclusions

High quality ResPes spectra of α-Pu and δ-Pu have been collected at the Advanced Light Source in Berkeley.   Supporting core level XAS and PES measurements have been made which confirm the α-Pu and δ-Pu are different but which also suggest the need for care in dealing with surface corruption.

VI   Acknowledgements

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